

METHOD FOR PREPARING OXYTITANIUM PHTHALOCYANINE
CHARGE GENERATING MATERIAL AND THE NEW-TYPE OXYTITANIUM
PHTHALOCYANINE CHARGE GENERATING MATERIAL THEREFROM

5 Technical Field

The present invention relates to a method for preparing oxytitanium phthalocyanine suitable as a charge generating material. More particularly, the present invention relates to a method for preparing oxytitanium phthalocyanine as a
10 charge generating material by appropriately mixing sulfuric acid with an oxytitanium phthalocyanine crude in a wet grinder, and an oxytitanium phthalocyanine charge generating material having a novel crystal form prepared by the method.

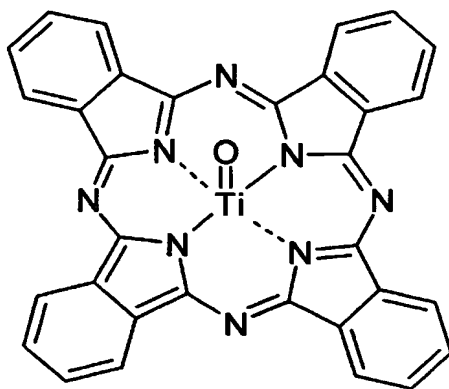
15 Background Art

Photoconductors are highly photosensitive in the visible region, and are widely used in various devices, such as copying machines, printers, etc. Most of the currently used photoconductors are produced by applying a photosensitive layer
20 including an inorganic charge generating material selected from selenium, zinc oxide, cadmium sulfide and others as a main component to a conductive substrate. However, these inorganic charge generating materials are still unsatisfactory in photosensitivity, thermal stability, water resistance, durability and other physical properties required in copying machines and printers. For example,
25 photoconductors using cadmium sulfide suffer from poor water resistance and

durability, and photoconductors using zinc oxide have a problem in terms of low durability. Further, photoconductors using selenium and cadmium sulfide are limited in their production and handling.

5 In an effort to solve the problems of the inorganic charge generating materials, a great deal of research has been conducted on organic charge generating materials. Of these, oxytitanium phthalocyanine is widely used due to its superior photosensitivity, durability, thermal stability, etc.

Oxytitanium phthalocyanine is commonly synthesized by reacting 1,2-dicyanobenzene or 1,3-diiminoisoindoline as a main material with titanium
10 tetrachloride or tetraalkoxy titanium as a titanium source in N-methylpyrrolidone, 1-chloronaphthalene or quinoline as a solvent at 160~200°C for 6~12 hours, and purifying the obtained reaction product. The final product is strictly defined as “oxytitanium phthalocyanine in a crude state (hereinafter, referred to as an “oxytitanium phthalocyanine crude”)”. Japanese Patent No. 62-256865 describes a
15 method for preparing an oxytitanium phthalocyanine crude by using 1,2-dicyanobenzene and titanium tetrachloride, U.S. Patent No. 4,971,877 describes a method for preparing an oxytitanium phthalocyanine crude by using 1,3-diiminoisoindoline and tetraalkoxy titanium, and *Bull. Chem. Soc. Jpn.*, 68, 1001-1005, 1995 reports a method for preparing an oxytitanium phthalocyanine crude by
20 using 1,2-dicyanobenzene and tetrabutoxy titanium. Since the oxytitanium phthalocyanine crudes cannot be directly used as charge generating materials due to their large particle size and poor electrophotographic characteristics, they must undergo an appropriate post treatment process in order to be used as highly photosensitive charge generating materials. The structural formula of oxytitanium
25 phthalocyanine is represented by the following Formula 1:

Formula 1

U.S. Patent No. 5,164,493 discloses a process for the preparation of oxytitanium phthalocyanine as a charge generating material which comprises dissolving an oxytitanium phthalocyanine crude in a mixed solution of trifluoroacetic acid and methylene chloride, and reprecipitating the solution in a mixed solution of methanol and water. The charge generating material thus prepared shows X-ray diffraction peaks at Bragg angles of $7.2 \pm 0.2^\circ$, $8.9 \pm 0.2^\circ$, $14.3 \pm 0.2^\circ$, $18.0 \pm 0.2^\circ$, $23.9 \pm 0.2^\circ$, $25.6 \pm 0.2^\circ$, $27.3 \pm 0.2^\circ$, $28.8 \pm 0.2^\circ$, $29.4 \pm 0.2^\circ$, and $36.4 \pm 0.2^\circ$. However, this process has the following disadvantages: i) large quantities of toxic gases are released due to the use of trifluoroacetic acid, ii) troublesome steps are involved, and iii) the high cost of trifluoroacetic acid results in high production costs.

U.S. Patent No. 5,252,417 discloses a process for preparing oxytitanium phthalocyanine as a charge generating material by using concentrated sulfuric acid, which is cheaper than trifluoroacetic acid. The charge generating material thus prepared shows X-ray diffraction peaks at Bragg angles of $7.2 \pm 0.2^\circ$, $9.1 \pm 0.2^\circ$,

11.2 \pm 0.2°, 13.5 \pm 0.2°, 14.4 \pm 0.2°, 24.0 \pm 0.2°, 27.2 \pm 0.2°, and 28.8 \pm 0.2°. According to this method, an oxytitanium phthalocyanine crude is dissolved in concentrated sulfuric acid in an amount of about 30~50 times the amount of the oxytitanium phthalocyanine crude, and the resulting solution is recrystallized from a solution of methanol and water. However, since an excessive amount of the sulfuric acid is used, costs required for neutralization are increased. In addition, since the crude must be dissolved at a temperature not higher than room temperature, there is a limitation in reducing the amount of the sulfuric acid to be used due to increased viscosity.

U.S. Patent No. 5,786,121 suggests a method for preparing oxytitanium phthalocyanine suitable as a charge generating material by mixing pentafluoropropionic acid and a halogenated alkane or halogenated aromatic compound, adding an aliphatic or aromatic sulfonic acid as an additive to the mixture to obtain an oxytitanium phthalocyanine crude, dissolving the oxytitanium phthalocyanine crude, and reprecipitating the solution in a mixed solution of water and methanol. However, since this method uses pentafluoropropionic acid, it produces much more toxic fumes than the method using trifluoroacetic acid. In addition, since the method uses difficult-to-handle and expensive raw materials, it is very dangerous and incurs considerable production costs.

Thus, there is a need for a method of preparing oxytitanium phthalocyanine usable as a high-quality charge generating material by using a cheap and easy-to-handle material, without the use of expensive and difficult-to-handle reactants, such as trifluoroacetic acid and pentafluoropropionic acid.

Disclosure of the Invention

Therefore, the present invention has been made in view of the above problems, and it is an object of the present invention to provide a method for preparing oxytitanium phthalocyanine as a high-quality charge generating material by using a cheap and easy-to-handle material.

It is another object of the present invention to provide an oxytitanium phthalocyanine charge generating material prepared by the method.

It is still another object of the present invention to provide a photoconductor produced using the oxytitanium phthalocyanine charge generating material.

In accordance with one aspect of the present invention, there is provided a method for preparing oxytitanium phthalocyanine as a charge generating material, comprising the steps of mixing 30~100wt% sulfuric acid and an oxytitanium phthalocyanine crude in a mixing ratio between 100:1 and 1:1, homogeneously grinding the mixture in a wet grinder filled with zirconia or glass beads as grinding media at -20°C~60°C for 0.1~24 hours, and removing the grinding media from the ground mixture using a solvent.

In accordance with another aspect of the present invention, there is provided an oxytitanium phthalocyanine charge generating material prepared by the method.

In accordance with still another aspect of the present invention, there is provided a photoconductor produced using the oxytitanium phthalocyanine charge generating material.

Brief Description the Drawings

The above and other objects, features and other advantages of the present

invention will be more clearly understood from the following detailed description taken in conjunction with the accompanying drawings, in which:

Fig. 1 is a graph showing the X-ray diffraction pattern of an oxytitanium phthalocyanine crude;

5 Fig. 2 is a graph showing the X-ray diffraction pattern of oxytitanium phthalocyanine prepared in Example 1 of the present invention;

Fig. 3 is a graph showing the X-ray diffraction pattern of oxytitanium phthalocyanine prepared in Example 2 of the present invention;

10 Fig. 4 is a graph showing the X-ray diffraction pattern of oxytitanium phthalocyanine prepared in Example 3 of the present invention;

Fig. 5 is a graph showing the X-ray diffraction pattern of oxytitanium phthalocyanine prepared in Comparative Example 1 of the present invention;

Fig. 6 is a graph showing the X-ray diffraction pattern of oxytitanium phthalocyanine prepared in Comparative Example 2 of the present invention;

15 Fig. 7 is a graph showing the X-ray diffraction pattern of oxytitanium phthalocyanine prepared in Comparative Example 3 of the present invention;

Fig. 8 is a graph showing the X-ray diffraction pattern of oxytitanium phthalocyanine prepared in Comparative Example 4 of the present invention;

20 Fig. 9 is a graph showing the X-ray diffraction pattern of oxytitanium phthalocyanine prepared in Comparative Example 5 of the present invention; and

Fig. 10 is a cross-sectional view of a photoconductor drum used for the measurement of the electrical properties of oxytitanium phthalocyanine in the present invention.

25 Best Mode for Carrying Out the Invention

Hereinafter, the present invention will be explained in more detail.

The present invention provides a method for preparing oxytitanium phthalocyanine as a charge generating material by mixing sulfuric acid and an oxytitanium phthalocyanine crude, grinding the mixture in a wet grinder filled with zirconia or glass beads as grinding media, and removing the grinding media from the ground mixture using a solvent.

The oxytitanium phthalocyanine crude used herein may be obtained by various processes commonly known in the art. For example, the oxytitanium phthalocyanine may be obtained by reacting 1,2-dicyanobenzene or 1,3-diiminoisoindoline as a main material with titanium tetrachloride or tetraalkoxy titanium as a titanium source in N-methylpyrrolidone, 1-chloronaphthalene or quinoline as a solvent at 160~200°C for 6~12 hours, and purifying the obtained reaction product. Fig. 1 shows the X-ray diffraction pattern of the oxytitanium phthalocyanine crude used in the present invention.

The sulfuric acid and the oxytitanium phthalocyanine crude are mixed in a mixing ratio between 100:1 and 1:1. The sulfuric acid preferably has a concentration of 30~100wt%. If the concentration of the sulfuric acid is below 30wt% or the mixing ratio of the sulfuric acid and the oxytitanium phthalocyanine crude exceeds 1:1, the oxytitanium phthalocyanine crude is not substantially dissolved in the sulfuric acid and agglomerated. Preferably, the sulfuric acid has a concentration of 50~80wt% and the mixing ratio of the sulfuric acid and oxytitanium phthalocyanine crude is in the range between 50:1 and 10:1.

As the grinder, there can be used: an agitation-type wet grinder, e.g., attritor, sand mill or pearl mill; a diffuser; a ball mill; or vibration mill.

As the grinding media, zirconia or glass beads can be used. The grinding temperature is in the range of -20°C ~ 60°C . When the grinding temperature is lower than -20°C or higher than 60°C , the oxytitanium phthalocyanine crude is not substantially dissolved in the sulfuric acid and further agglomerated or decomposed.

5 The grinding is preferably carried out at a temperature of 0°C ~ 25°C . The grinding time is 0.1~24 hours. Within this range, the sulfuric acid and the oxytitanium phthalocyanine crude are homogeneously ground. It is preferable to grind the mixture for 3~5 hours.

After completion of the grinding, the solvent is used to remove the grinding
10 media from the ground mixture. For example, the solvent is added to the ground mixture in a ratio of 1:4 to dissolve the ground mixture, thereby forming a slurry. Thereafter, the slurry is filtered, washed, and dried at 40 ~ 80°C for 3~20 hours. At this time, the washing is preferably carried out until the filtrate is neutralized (a pH of at least 7.0).

15 Examples of preferred solvents include water, aliphatic alcohols, e.g., methanol and ethanol, ketones, e.g., acetone, methyl ethyl ketone and tetrahydrofuran, and mixtures thereof.

The oxytitanium phthalocyanine charge generating material prepared by the method of the present invention shows broad X-ray diffraction peaks at Bragg
20 angles of $6.8 \pm 0.2^{\circ}$ to $10.0 \pm 0.2^{\circ}$, and particularly the highest peak appears at a Bragg angle of $8.8 \pm 0.2^{\circ}$.

In addition to these peaks, the oxytitanium phthalocyanine charge generating material shows X-ray diffraction characteristic peaks at Bragg angles of $14.2 \pm 0.2^{\circ}$, $24.0 \pm 0.2^{\circ}$ and $27.2 \pm 0.2^{\circ}$, or at Bragg angles of $7.2 \pm 0.2^{\circ}$, $9.2 \pm 0.2^{\circ}$,
25 $10.0 \pm 0.2^{\circ}$, $11.3 \pm 0.2^{\circ}$, $13.7 \pm 0.2^{\circ}$, $17.8 \pm 0.2^{\circ}$, $18.5 \pm 0.2^{\circ}$, $23.0 \pm 0.2^{\circ}$, $24.8 \pm$

0.2°, 27.2 ± 0.2° and 28.8 ± 0.2°, or at Bragg angles of 7.5 ± 0.2°, 11.4 ± 0.2°, 13.7 ± 0.2°, 14.8 ± 0.2°, 18.0 ± 0.2°, 18.8 ± 0.2°, 23.0 ± 0.2°, 25.1 ± 0.2°, 27.2 ± 0.2° and 28.8 ± 0.2°. The oxytitanium phthalocyanine charge generating material shows the strongest X-ray diffraction peak at a Bragg angle of 27.2 ± 0.2°. The oxytitanium phthalocyanine charge generating material can be effectively used in the production of photoconductors, particularly organic photoconductors.

The present invention will now be described in more detail with reference to the following examples and comparative examples. However, these examples are not to be construed as limiting the scope of the invention.

Example 1

720ml of zirconia beads were introduced into a 0.5 gallon attritor (Union Process, USA), and then 300ml of 70wt% sulfuric acid and 50g of an oxytitanium phthalocyanine crude were added thereto. Thereafter, the mixture was ground for 5 hours while the temperature of the grinder was maintained at room temperature or less. After completion of the grinding, 2,000ml of water was added to dilute the ground mixture, and then the zirconia beads were separated from the ground mixture. The remaining slurry was filtered, washed with water until the filtrate was neutralized, and dried in a drier at 60°C to yield 48.8g of an oxytitanium phthalocyanine charge generating material. The X-ray diffraction pattern of the oxytitanium phthalocyanine was obtained under the following conditions:

X-ray bulb: Cu

Cu K-alpha wavelength (Å): 1.54056

Voltage (kV): 40.0

Current (mA): 100.0

Starting angle ($^{\circ}$ 2 Theta): 5.00

Stopping angle ($^{\circ}$ 2 Theta): 45.00

Stepping angle ($^{\circ}$ 2 Theta): 0.020

5 The X-ray diffraction pattern of the oxytitanium phthalocyanine charge generating material is shown in Fig. 2.

Example 2

48.4g of an oxytitanium phthalocyanine charge generating material was prepared in the same manner as in Example 1, except that a mixture (1:1) of water
10 and methanol as a solvent for separating the zirconia beads was used. The X-ray diffraction pattern of the oxytitanium phthalocyanine charge generating material is shown in Fig. 3.

Example 3

15 48.4g of an oxytitanium phthalocyanine charge generating material was prepared in the same manner as in Example 1, except that a mixture (7:3) of water and methanol as a solvent for separating the zirconia beads was used. The X-ray diffraction pattern of the oxytitanium phthalocyanine charge generating material is shown in Fig. 4.

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Comparative Example 1

300ml of 70wt% sulfuric acid was placed in a beaker, and stirred using a magnetic stirrer while the temperature was maintained at 10°C or less. 50g of an oxytitanium phthalocyanine crude was added to the beaker while maintaining the
25 temperature, and the mixture was then stirred for 5 hours. Thereafter, 2,000ml of

water was added to dilute the mixture, filtered, washed with water until the filtrate was neutralized (a pH of at least 7.0), and dried in a drier at 60°C to yield 48.7g of oxytitanium phthalocyanine. The X-ray diffraction pattern of the oxytitanium phthalocyanine is shown in Fig. 5.

5

Comparative Example 2

48.6g of oxytitanium phthalocyanine was prepared in the same manner as in Comparative Example 1, except that a mixture (1:1) of water and methanol was used instead of water. The X-ray diffraction pattern of the oxytitanium phthalocyanine is shown in Fig. 6.

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Comparative Example 3

48.6g of oxytitanium phthalocyanine was prepared in the same manner as in Comparative Example 1, except that a mixture (7:3) of water and methanol was used instead of water. The X-ray diffraction pattern of the oxytitanium phthalocyanine is shown in Fig. 6.

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Comparative Example 4

10g of an oxytitanium phthalocyanine crude was dissolved in a mixed solution of 20ml of trifluoroacetic acid and 80ml of dichloromethane, and stirred for 15 min. After stirring, 500ml of methanol and 500ml of water were added to the mixture, stirred for 45 minutes, and left to stand for 25 minutes. Thereafter, the supernatant was removed, followed by the addition of methanol (400ml). The resulting slurry was stirred for one hour, filtered, and washed with methanol (20ml x 2), water (20ml x 2), water (100ml x 1) and methanol (40ml). The washed slurry

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was dried in a drier at 60°C to yield 9.6g of oxytitanium phthalocyanine. The X-ray diffraction pattern of the oxytitanium phthalocyanine is shown in Fig. 8.

Comparative Example 5

5 10g of an oxytitanium phthalocyanine crude was dissolved in 500g of 96% sulfuric acid while the temperature was maintained at 5°C or less, and the mixture was then stirred for 2 hours at this temperature. After stirring, the sulfuric acid solution was added to a mixed solution of water (2,000g) and methanol (2,000g) while the temperature was maintained at -20°C or less, and was then stirred for 15
10 minutes at this temperature. The resulting mixture was filtered, washed with methanol and 1% ammonia water, sequentially, and finally washed with water until the filtrate was neutralized (a pH of at least 7.0). The washed mixture was dried in a drier to yield 9.5g of oxytitanium phthalocyanine. The X-ray diffraction pattern of the oxytitanium phthalocyanine is shown in Fig. 9.

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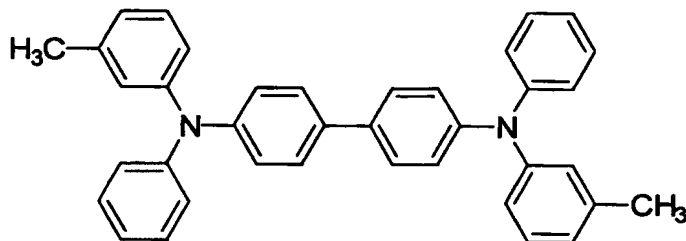
Test Example 1

2.0g of the oxytitanium phthalocyanine prepared in Example 1, 1.0g of polyvinylbutyral, 40g of tetrahydrofuran, and 110g of glass beads (diameter: 1mm) were dispersed in a paint shaker for 5 hours, and then 150g of tetrahydrofuran was
20 added thereto. The mixture was further dispersed for 10 minutes to prepare a coating solution for a charge generating layer. The coating solution was coated on the surface of an oxide film-coated aluminum drum to a thickness of 0.2μm, and dried in a drier at 120°C for 5 minutes.

Separately, 25g of N,N'-bis(3-methylphenyl)-N,N'-diphenylbenzidine
25 (Formula 2) and 25g of poly(4,4-cyclohexylidene diphenylene carbonate) (Formula

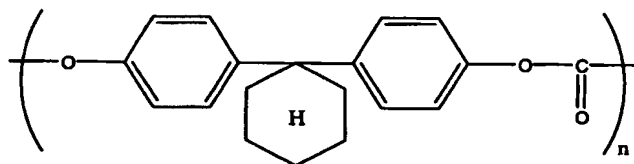
3) were dissolved in 200g of monochlorobenzene to prepare a coating solution for a charge transport layer.

Formula 2



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Formula 3



10 The coating solution for a charge-transport layer was coated on the charge generating layer-coated aluminum drum, and dried in a drier at 120°C for 30 minutes to form a 20μm thick charge transport layer, thereby producing a photoconductor drum.

15 The electrophotographic characteristics of the photoconductor drum were determined using an analyzer PDP-2000 (Quality Engineering Associates Inc., USA) in accordance with the following procedures.

1) Initial surface potential (VDDP)

When the photoconductor drum was charged by corona discharge at -60 kV, a potential generated on the surface of the photoconductor drum was measured.

2) Dark decay (DD5)

3 seconds after the surface of the photoconductor drum was charged with a voltage of -700V, change in the potential of the drum surface was measured. The dark decay (DD5) was expressed in percent relative to the initial surface potential

DD5 (%) = (surface potential 3 seconds after charging/initial surface potential) x 100

3) Sensitivity (E50%)

After the surface of the photoconductor drum was charged with a voltage of -700V and was then exposed to monochromatic light of a wavelength of 750nm, the intensity of the monochromatic light required to reduce the surface potential of the drum to half of the initial surface potential of the drum was determined.

4) Final potential (VF)

After the surface of the drum was charged with a voltage of -700V and was exposed to monochromatic light of a wavelength of 780nm and an intensity of 13 J/cm², the surface potential was measured.

The obtained results are summarized in Table 1.

Test Examples 2 and 3

The procedures of Test Example 1 were repeated, except that the oxytitanium phthalocyanine charge generating materials prepared in Examples 2 and 3 were used. The results are summarized in Table 1.

Test Examples 4 to 8

The procedures of Test Example 1 were repeated, except that the oxytitanium phthalocyanine charge generating materials prepared in Comparative Examples 1 to 5 were used. The results are summarized in Table 1.

Table 1

5 Measurement results of electrophotographic characteristics

Test Example No.	Charge generating material	VDDP (V)	DD5 (%)	E50% (J/cm ²)	VF (V)
1	Example 1	-666	92.0	0.101	-64
2	Example 2	-682	90.2	0.108	-49
3	Example 3	-674	90.6	0.111	-54
4	Comparative Example 1 *	-502	70.1	0.508	-108
5	Comparative Example 2	-602	79.1	0.378	-66
6	Comparative Example 3	-619	81.2	0.412	-74
7	Comparative Example 4	-600	62.0	0.130	-46
8	Comparative Example 5	-627	75.1	0.185	-108

10 * Because the drum surface was not charged to a voltage of -700V, the voltage of the corona charger was set to 7.45kV for the measurement of the electrophotographic characteristics.

Industrial Applicability

As apparent from the above description, according to the method of the

present invention, since the combination of sulfuric acid and the wet grinder can markedly lower the concentration and amount of the sulfuric acid used, costs required for neutralization of waste sulfuric acid can be greatly reduced. In addition, oxytitanium phthalocyanine usable as a high-quality charge generating
5 material can be prepared without the use of expensive and difficult-to-handle reactants, such as trifluoroacetic acid and pentafluoropropionic acid.

Although the preferred embodiments of the present invention have been disclosed for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the
10 scope and spirit of the invention as disclosed in the accompanying claims.